Handout on Isotopes and Climate

EES 3310/5310 Global Climate Change

Reading for Friday, February 7

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Introduction

One of the most difficult problems climate scientists wrestle with is how to test theories about climate and climate change when there is no opportunity to perform controlled experiments, as laboratory scientists can do. When experiments are not possible, scientists must rely on observation, but because the climate changes so slowly, with important feedback systems operating only on time scales of centuries, millennie, or even hundreds of thousands of years climate scientists cannot rely on human observations to test their theories.

The first thermometers accurate enough for weather and climate measurements were invented in the early 18th century, and around 1816 the first crude attempts were made to map out weather patterns by comparing thermometers at different locations. Not until the mid-19th century were enough meteorologists were making measurements at enough places around the world that climate scientists today can reconstruct global average temperatures from their historical measurements. Thus, if we want to know about temperatures more than 160–200 years ago, we cannot rely on people directly measuring the weather, but must look for what climate scientists call **proxy data** recorded in the geological record that will tell us about past climates.

There are many kinds of proxy data for climate, and long textbooks have been written about them.[*] Different plants flourish in different conditions: wet vs. dry, warm vs. cold, etc. Pollen from many plants is very durable and can be used to infer past climatic conditions if scientists can assign a reliable date to the pollen. Similarly, when trees are growing in stressful conditions, such as high on mountains, slight temperature changes can have big effects on their growth, so scientists can look at the widths of tree rings to identify warmer and cooler seasons and to identify trends of warming and cooling. Some trees can live for many thousands of years[†]

[*] Two excellent books, if you are interested, are Bradley 1999 and Cronin 2013.

[†] The oldest living thing that we know of is a bristlecone pine tree in California, which is more than 5,000 years old. Five giant sequoia trees, also in California, are known to be more than 3000 years old.

But perhaps the most valuable tool for paleoclimatologists is the chemical study of isotopes. A series of discoveries between 1913 and 1919 demonstrated that the atomic elements from which all matter is made came in isotopic varieties. The chemical properties of an element are determined by the electric charge of the atom's nucleus, but scientists discovered that a single element, such as carbon, came in several isotopes, all chemically identical, but each with a slightly different mass.

Using isotopes as proxy records for paleoclimate was discovered by Harold Urey (1893–1981) in the late 1940s and early 1950s. Urey had won the Nobel Prize in 1934 for discovering that hydrogen had different isotopes* After World War II, Urey began looking for applications of isotopes to practical questions. Urey and others had determined that while different isotopes of the same element would undergo the same reactions and form the same compounds, the rates of the reactions would be slightly different and the relative rates would depend on temperature. Urey and his colleagues applied that knowledge to oxygen isotopes and figured out that the ratio of different isotopes of oxygen in minerals from geological specimens could be used to determine the temperature at which the mineral had formed. In 1951, they published an analysis of a 100-million year old fossil shell, showing that they could measure the seasonal temperature variations over the animal's four-year life.

Isotope Basics

An atom's chemical element is determined by the electric charge of its nucleus. This is what the chemical symbol (e.g., H for hydrogen, O for oxygen, C for carbon) indicates. The atom's weight (in atomic mass units) determines its isotope. The most common isotope of hydrogen has a mass of 1, and is written ^{1}H. Its heavier stable isotope, deuterium, has a mass of 2 and is written ^{2}H or as D (for deuterium). There are many isotopes of many elements, but for this handout we will look only at six stable isotopes (two each of hydrogen, carbon, and oxygen) and one unstable isotope of carbon. The most common form of oxygen is ^{16}O, but about 0.2% of oxygen atoms are ^{18}O. The most common isotope of carbon is ^{12}C, with a mass of 12, but about 1% of all carbon atoms are the heavier isotope carbon-13 (^{13}C).

In addition, about one one-trillionth (10^{-12}) of all carbon atoms in the atmosphere are an unstable radioactive form called carbon-14 (^{14}C), which decays and turns into nitrogen atoms with a characteristic time, called a half-life, of about 5700 years, so that over successive half-lives an original sample of N ^{14}C atoms will diminish to $N/2$, $N/4$, and $N/8$, at 5700 years, 11,400 years, and 17,100 years; and so on. After about 10 half-lives the ^{14}C remaining in a typical sample will be too small to detect.

Climate scientists use stable isotopes to learn about past temperatures and they use radioactive isotopes to tell how old things are. Combining stable isotopes and radioactive isotopes, they can infer the temperature at which a specimen was created and when it was created, thus pinning down a time and temperature from an ancient climate.

Delta notation

This section is here to explain the delta-notation used by climate scientists in measuring isotopes. I am including it because you will see delta notation on charts, but I will not ask you to do calculations using the mathematical formula in Equation 1

All you need to know is that larger values of δ mean higher concentrations of the isotope in question and smaller values mean lower concentrations.

Measurements of isotope concentrations in specimens are usually reported using **delta notation**: First, scientists measure the ratio of the rare isotope to the more common one. Then they compare that to a **standard ratio**, which represents some reference material. Then they report the isotope ratio in their specimen as

$$\delta^{18}\mathrm{O} = \left(\frac{(^{18}\mathrm{O}/^{16}\mathrm{O})_{\text{specimen}} - (^{18}\mathrm{O}/^{16}\mathrm{O})_{\text{standard}}}{(^{18}\mathrm{O}/^{16}\mathrm{O})_{\text{standard}}}\right) * 1000‰ \tag{1}$$

*Normal hydrogen has an atomic mass of 1, but about one out of every 6000 hydrogen atoms has mass 2 and is called **deuterium**.

Isotopes and Temperature

Both hydrogen and oxygen isotopes are commonly used to infer temperature. Hydrogen isotopes are used most commonly as a proxy measurement for ancient ice samples from glaciers, to infer the air temperature at the time the snow fell that became a layer of ice. Oxygen isotopes are used as proxies for ice temperature but oxygen isotopes in coral reefs, sea shells, and the mineral skeletons of microscopic plankton can also be used as proxies for sea-surface temperature. Finally, through an indirect chain of reasoning, oxygen isotope ratios in the skeletons of deep-sea (benthic) organisms can be used to trace ancient sea levels.

Ancient ice temperatures

Water molecules can contain different isotopes of hydrogen and oxygen. The vast majority of water molecules contain two ^{1}H atoms and one ^{16}O atom, but a small fraction contain one or two ^{2}H atoms and/or a ^{18}O atom. All of these variants are slightly heavier than common water. Climate scientists concentrate on three of the possible combinations: $^1H_2{}^{16}O$, $^1H^2H^{16}O$, and $^1H_2{}^{18}O$

Whether they are liquid or vapor, water molecules are constantly moving, vibrating, and bouncing around. Lighter molecules move faster at a given temperature, and that higher speed makes lighter molecules of liquid water more likely to escape from a liquid surface and evaporate into the atmosphere. It also makes lighter molecules of water vapor less likely to stick together and form liquid droplets. Thus, at any temperature, water vapor over the ocean will have a smaller fraction of the heavy ^{2}H or ^{18}O atoms than the liquid ocean.

This difference, in itself, tells us nothing about temperature, but it turns out that the relative rate of evaporation of heavy and light water molecules depends on temperature: The colder the temperature, the farther apart the evaporation rates for heavy and light molecules are from one another, and the higher the temperature, the closer the rates are to one another. Thus, by comparing the ratio of heavy and light water in the vapor over the ocean, we can learn something about the air temperature. Higher temperatures will correspond to higher ratios of ^{2}H or ^{18}O.

However, we do not have samples of water vapor from over the ocean thousands of years ago. We have samples of ice from glaciers. As water vapor travels, blown by winds, from the ocean to locations far inland in Greenland and Antarctica, the isotopic composition is constantly changing because some of the water vapor condenses along the way and falls as rain or snow.

As the wind blows air from the source region of the ocean, rain and snow fall (see Figure 1). Precipitation contains higher fractions of water with the heavier isotopes (^{2}H and ^{18}O) than the air does, so as snow and rain fall out of the air, the fraction of heavy isotopes in the remaining water vapor diminishes. This means that as the air gets closer to the poles, or further from the coast, less water vapor with heavy isotopes remains in the atmosphere, so precipitation that falls closer to the poles or farther from the coast will have lower values of δ^2H and δ^{18}O. This effect depends on the air temperature: the drop in δ^2H and δ^{18}O is more rapid at colder temperatures and slower at higher temperatures, so **for locations far from the ocean source, higher values of δ^2H and δ^{18}O correspond to warmer air and lower values correspond to cooler air.**

The isotopes ratios in snow and ice depend on two temperatures: the sea-surface temperature where the water vapor originally evaporated and also the air temperature over the land. It might seem impossible to separate the two, but scientists can compare ratios of different isotopes: The relationship between sea-surface temperature in the source region and air temperature at the glacier site is different for hydrogen and oxygen, so by using both isotopes together, scientists can unscramble the competing effects of distant sea-surface temperature and local air temperature to arrive at a reliable measurement of the local air temperature.

Scientists want to be careful that they aren't making errors, so they check isotopic measurements not only against one another but also against the historical record as far back as that goes (around 160 years), and with older samples they check one ice core against another: Does ice from different parts of Antractica or different parts of Greenland show consistent temperature patterns? Do temperatures inferred from isotopic ratios in the ice agree with temperatures inferred from different kinds of proxy data?

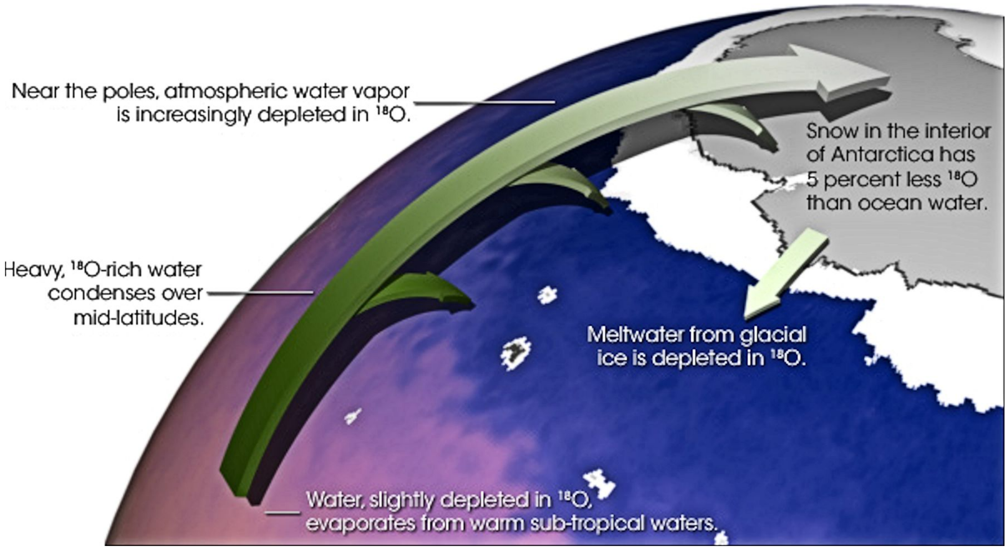


Figure 1: As winds carry air away from the ocean source region, the farther from the source region it goes, the less ^{18}O it contains.

Figure 2a shows, that isotopes show consistent patterns of variation with the average annual temperatuyre for both Antarctica (using hydrogen isotopes) and Greenland (using oxygen isotopes). Figure 2b shows that comparing oxygen isotope ratios to average annual temperatures at many places around the world also produces very consistent results. The fact that in both figures, the measured points all lie very close to straight lines provides strong evidence that isotopes can give consistent and reliable temperature readings. This pattern does not prove by itself that isotope ratios are reliable thermometers, but together with a lot more evidence that goes beyond the scope of this class, scientists have concluded that isotope ratios, when used carefully, provide very reliable measurements of past temperatures.

Beyond ice

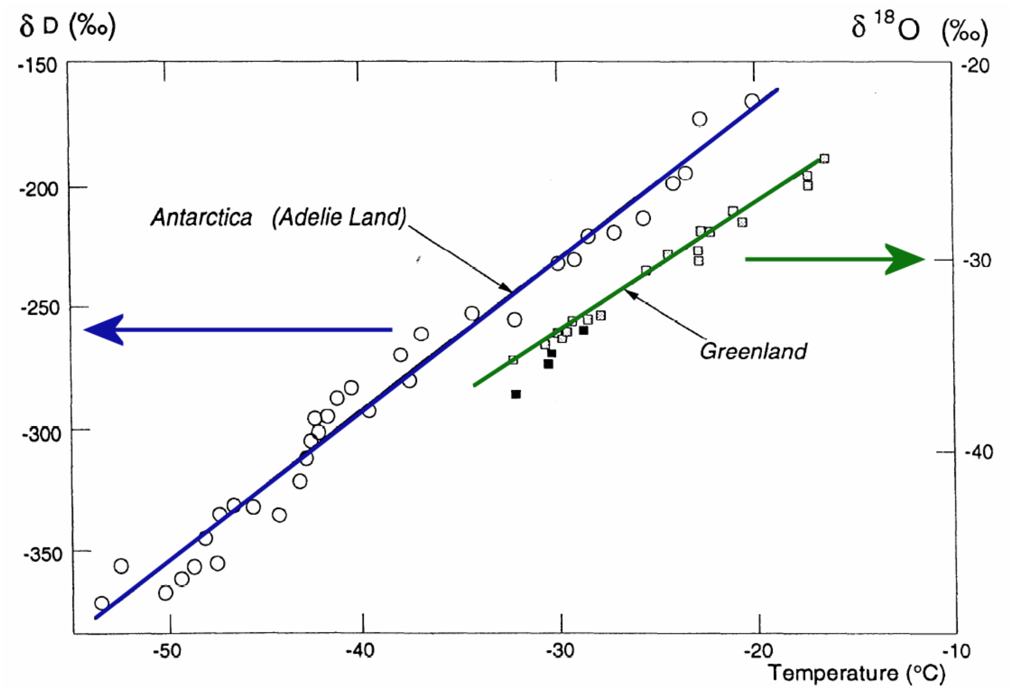
Oxygen and hydrogen isotope ratios can tell us the air temperature when snow fell that later became a layer of ice in a glacier or ice cap. This has been applied to the giant ice caps on Greenland and Antarctica, but it has also been used with other kinds of samples.

Stalagmites and stalactites in caves (known collectively as speleothems) grow with annual layers as water drips on them with seasonal variations and deposits minerals. Counting layers on a speleothem allows scientists to determine the age of a given layer, and chemical analysis of isotopes can give information about the climate when that layer was deposited. Prof. Jessica Oster at Vanderbilt's Earth & Environmental Sciences Department is using isotope ratios in speleothems to study past climate change and ancient weather patterns in North America and South Asia.

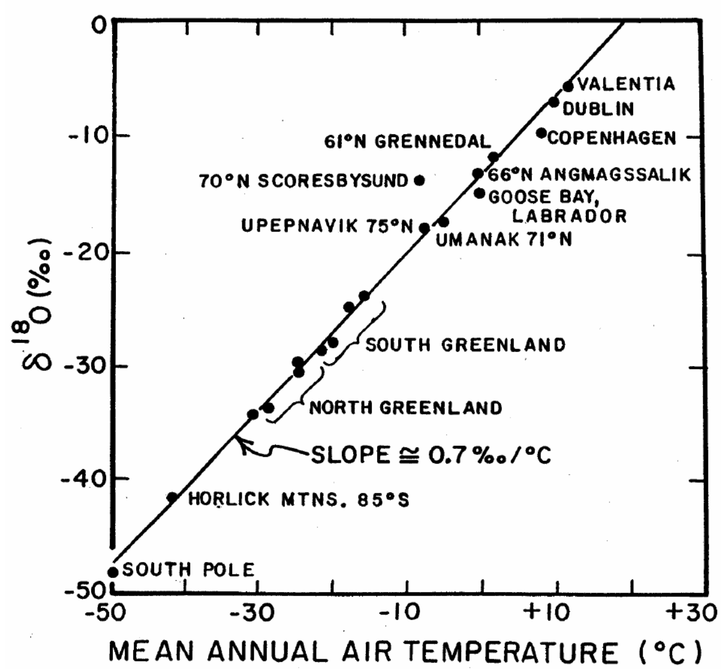
Scientists can also use skeletal remains of biological organisms to determine the temperature of their environment. Corals, shellfish, microscopic plankton, and other organisms that produce mineral bones, shells, and teeth incorporate oxygen from the environment and the ratio of ^{18}O to ^{16}O in these body parts can tell us about the temperature of the environment in which the organism lived.

Here, I will focus on marine animals and plants, but Prof. Larisa DeSantis at Vanderbilt's Earth & Environmental Sciences Department uses isotopes in the teeth of ancient mammals to understand their diets, the climates in which they lived, and what caused extinctions and Prof. Tiffiny Tung in Vanderbilt's Anthropology Department analyzes oxygen isotopes from teeth and bones of animal and human teeth and bones, collected at archeological sites to learn about migration patterns and how climate change affected ancient civilizations.

Coral reefs grow annual layers of carbonate material, so just as scientists can use the layers of ice



(a) Calibration of temperatures using hydrogen and oxygen isotopes at many sites in Greenland and Antarctica. The data from Antarctica shows temperature versus $\delta D = \delta^2$H (plotted on the left-hand scale) and the data from Greenland shows temperature versus δ^{18}O (plotted on the right-hand scale). From Jouzel et al. 1997.



(b) Calibrating temperatures using oxygen isotopes at many sites around the world., from Broecker 2002.

Figure 2: Calibrating ice-core temperatures using isotopes. Average annual temperatures measured with thermometers are plotted against isotope ratios. The closer all the points fall to the straight lines, the more accurate isotopes are at measuring temperatures at other places and times.

in glaciers to extract material of a known age, they can similarly use layers of corals to count years, and extract samples corresponding to specific years in the past.

Many kinds of plankton grow mineral skeletons, consisting of either SiO_2 or $CaCO_3$. When these plankton die, their skeletons sink to the bottom of the ocean and are can be preserved, mixed in with mud and other sediments. The oxygen isotopes in these skeletons can tell us about the temperature of the ocean surface at the time they lived.

Isotopes and Sea Level

Oxygen isotopes do not only tell us about temperature. They can also tell us about sea level. When water evaporates from the oceans, it carries extra ^{16}O and leaves behind an ocean enriched in ^{18}O. If the evaporated water falls as rain, it runs back to the oceans and replenishes the ^{16}O, but if it falls as snow on giant glaciers and does not melt, the sea level will drop as glaciers grow during ice-age cycles. The bigger the glaciers, the higher the fraction of ^{18}O in the oceans.

Miles down, at the bottom of the oceans, the water temperature does not change very much. It is perpetually slightly above freezing, so changes in oxygen isotope ratios in creatures that live deep in the oceans (**benthic orgamisms**) will not reflect the water temperature but the overall concentration of oxygen isotopes in the oceans. Larger values of $\delta^{18}O$ in the skeletons of benthic organisms, the lower the sea level and the larger the ice caps and glaciers covering the land surface.

You may think about my earlier comment that you can tell past sea surface temperatures from skeletons of organisms that live near the sea surface and ask why they wouldn't also be affected by the changes in oxygen isotopes due to rising and falling sea levels. The answer is that they are, so using near-surface organisms as proxies for past sea surface temperatures requires very careful measurements to account for both temperature changes and sea-level changes.

Carbon Isotopes

Carbon isotopes are not used to measure ancient temperatures, but are used to understand other aspects of the environment. One of the most important is determining what is causing the atmospheric concentration of CO_2 to grow.

It turns out that just as lighter isotopes in water are more prone to evaporate, lighter isotopes of carbon are more prone to be converted from CO_2 to sugar by photosynthesis. Thus, organic forms of carbon that are produced by photosynthesis will have a smaller ratios of ^{13}C (i.e., $\delta^{13}C < 0$). Measurements of $\delta^{13}C$ in atmospheric CO_2 show that $\delta^{13}C$ is negative and is becoming more negative at the same rate that atmospheric CO_2 concentrations are growing. This is powerful evidence that atmospheric CO_2 comes from biological sources, not mineral sources, and thus cannot be coming from volcanic outgassing.

In other aspects of environmental science, $\delta^{13}C$ is different in the tissues of different kinds of plants, and when animals graze on different plants, the $\delta^{13}C$ in their bodies, bones, and teeth can reflect the plants they ate. Thus, scientists can use careful measurements of $\delta^{13}C$ to determine what ancient animals ate. Knowing whether they ate plants characteristic of lush forests or arid grasslands can tell us about the environment in which they flourished, even if all we have to go on is preserved bones and teeth.

Unstable Isotopes and Time

Most of this handout has focused on using stable isotopes to determine past temperatures, sea levels, etc. But unstable isotopes are also very valuable to earth and environmental scientists.

Unstable isotopes are isotopes that are radioactive. They decay over time into different elements at very precisely defined rates. If we know what the ratio of an unstable isotope to stable ones was when a specimen was formed, then measuring the ratio today can tell us a lot about the age of the specimen. Many unstable isotopes are used for establishing the age of rocks and other things, but here we will focus on ^{14}C (carbon-14). Carbon-14 is created by cosmic rays from space colliding at high energy wtih nitrogen atoms high in the atmosphere. Carbon-14 has a a half-life of about 5700 years, so every 5700 years half of the ^{14}C atoms in a specimen will decay, turning back into nitrogen atoms. 5700 years after a specimen is formed, it will have half the amount of ^{14}C that it had when it was fresh. After another 5700 years, it will have a quarter as much as it originally did. After another 5700 years, it will have one eighth, and so on, with the remaining ^{14}C dropping by a factor of two every 5700 years.

Scientists measuring ancient climates using stable isotopes in glaciers, corals, speleothems, and other materials often use unstable isotopes to check the age of their samples. When the samples have well-defined layers, such as tree rings, layers of ice in glaciers, layers of coral and speleothems, or sedimentary laminations from the bottom of lakes, they can cross-check ^{14}C ages with their count of the layers to make sure that everything is consistent.

Summary

In the 1930s, Milutin Milankovitch developed his theory that variations in Earth's orbit caused the cycle of the ice ages over the past 2.75 million years, but there was no way to test this theory. One of the big impediments was the inability to determine when the ice ages occurred with enough accuracy to see whether they lined up with Milankovitch's orbital cycles.

In the 1970s, scientists devised ways to use oxygen-isotope analysis of sediments recoverd from the ocean floor around the world to precisely determine when the sea level rose and fell and when the climate warmed and cooled. This provided the first clear evidence that the ice ages followed the timing Milankovitch had predicted (Hays, Imbrie, and Shackleton 1976). In the 1980s and 90s, scientists developed ways to apply these techniques to glaciers with great precision, combining oxygen isotope and hydrogen isotope analysis to develop two independent ways to measure temperature (this way they could check for consistency between the two techniques) and using a number of different techniques, including counting layers and analyzing ^{14}C ratios, to determine the age of ice layers.

This finally presented a precise record of temperature over hundreds of thousands of years. Some of the most exciting discoveries were that temperatures in Greenland and Antarctica, half a planet apart, showed remarkable synchronization, proving that the ice ages were truly global events and finding that while the overall structure of the ice ages followed very slow processes taking tens or hundreds of thousands of years, there were also many episodes where global temperatures changes dramatically in as little as a decade. This raised fresh concerns about tipping points in the earth's climate system that might cause the global warming we are currently experiencing to produce similar large and abrupt changes at some point in the future.

No one knows whether such events are likely, but if they occur they could be severe because they would happen too fast for people to adapt to them or reverse them. Thus, research on abrupt climate change is a very active are these days.

Review of key points

- Lighter isotopes evaporate faster from oceans.
- Therefore, snow and ice on land has lighter H and O isotopes than sea water.
- As the total amount of snow and ice on land gets larger (e.g., during an ice age), two things happen:
  1. Sea level drops
  2. Sea water becomes isotopically heavier (the concentration of heavy isotopes, such as ^{18}O gets larger)

  Thus, higher values of δ^{18}O in deep sea water indicate lower sea level and larger glaciers on land.

- Isotope ratios in snow and ice recovered from glaciers depends on three things: the sea-surface temeprature where the water evaporated, the air temperature over the land, and how far from the ocean source the snow fell.
- In general, larger values of δ^2H and δ^{18}O in glacial ice from Greenland and Antarctica correspond to higher air temperatures.

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